Parametric study of perovskite solar cells using drift-diffusion modelling

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Motivation

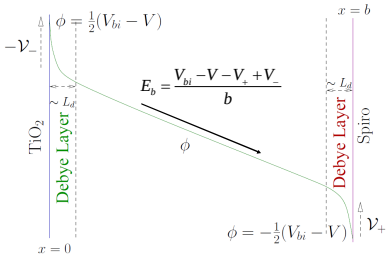
We have developed a drift-diffusion model of perovskite solar cells that includes the effect of moving ions and is therefore able to predict hysteresis curves similar to those observed in measurements. This model can be used to investigate the effect of different types of ions and different recombination mechanisms.

Conclusions

1. Our drift-diffusion model of perovskite cells with moving ions predicts hysteresis similar to that observed in measurements
2. Asymptotic model validated by numerical simulation
3. I^- vacancies are the most convincing candidate for the main mobile ion species
4. Assuming linear hole-dependent recombination in the bulk and at the TiO_2 interface yields a good fit to measurement

Asymptotic approximation

Mean ion density $N_0 \sim 10^{-19}$ cm^{-3} [1], making problem too stiff for numerics. However, if the density of ions is that large, it can be assumed that all of the charge accumulates in small Debye layers, causing significant electrostatic potential jumps $V_\pm$ in the Debye layers & constant electric field E_b in the bulk. This neglects the contribution of electrons & holes, which is valid for $V < V_{bi}$.



Assuming the main moving ion species to be positively charged I^- vacancies [2], the surface charge $Q_\pm$ in the Debye layers is given by

$$Q_\pm = \pm\sqrt{2q\varepsilon N_0 V_T\left[\exp\left(\frac{V_\pm}{V_T}\right) - 1 - \frac{V_\pm}{V_T}\right]}$$

Figure 1 *Simulation domain. The two Debye layers and the bulk form three subdomains.*

[1] Aron Walsh *et al.*, *Angewandte Chemie* (2015), Vol. 127, 1811-1814.
[2] C. Eames *et al.*, Nature Communications (2015), Vol. 6, 7497.

Testing the asymptotics

To test the asymptotic approximation, a numerical calculation (solid blue lines) was performed for a smaller ion density $N_0 = 10^{17}$ cm^{-3}, scanning from $V = V_{bi} = 1$ Volt to short circuit then back again. The same calculation was performed with the asymptotic model (dashed green lines).

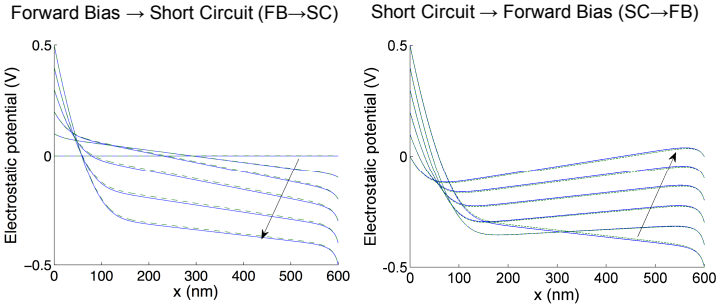


Figure 2 *Time evolution of potential in the perovskite film, calculated with a numerical simulation (solid blue lines) and the asymptotic approximation (dashed green lines).*

Recombination mechanisms

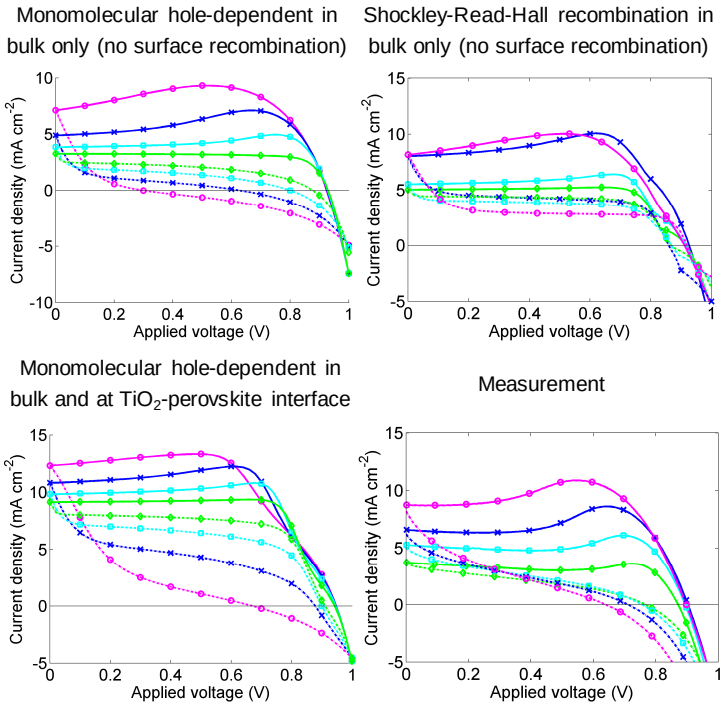


Figure 3 *Calculated current-voltage curves for three recombination mechanisms, with a set of measured curves for comparison. Scan rates are 1 V/s (magenta circles), 500 mV/s (blue crosses), 250 mV/s (cyan squares) and 100 mV/s (green diamonds). Solid lines denote FB→SC scans; broken lines denote SC→FB scans.*

Nature of the moving ions

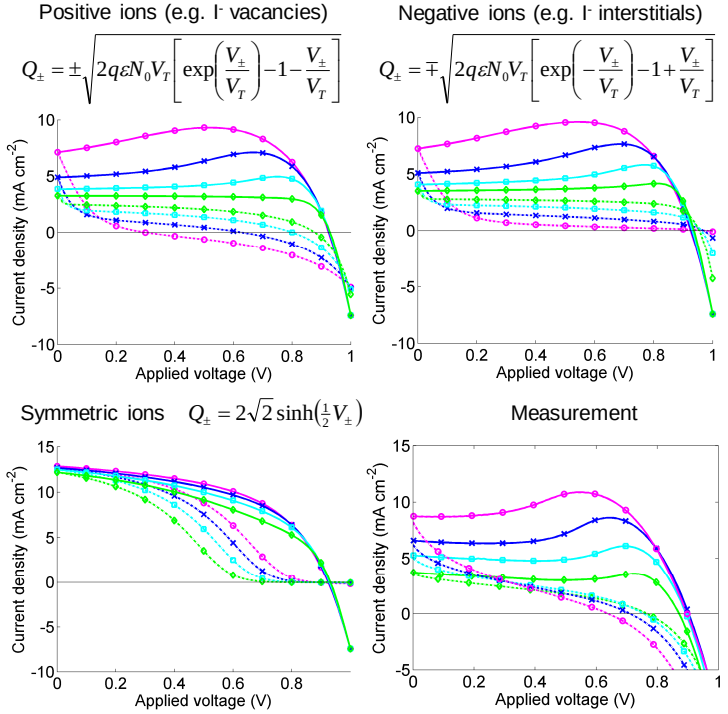


Figure 4 *Calculated current-voltage curves for three types of mobile ion system, with a set of measured curves for comparison. Scan rates as in Figure 3. A diffusion coefficient of 10^{-11} cm^2/s is assumed for all ions. A monomolecular hole-dependent recombination scheme in the bulk was assumed, with no surface recombination.*